PYROLYSIS OF AGRICULTURAL WASTE: EFFECT OF CATALYST APPLICATION

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ABSTRACT

Fuel gas can be produced from the pyrolysis process of biomass. Fuel gas is a clean and renewable energy thus becoming a very suitable energy that can replace the fossil fuels for example hydrogen and methane. The abundant quantity of agricultural waste in Malaysia especial palm oil waste made this process even more promising. This research is aimed to produce high yield of fuel gas with a coke resistance catalyst. Palm oil wastes were used as samples in this research which are empty fruit bunch (EFB) and palm oil fibre (POF). The catalysts used were nickel alumina, doped with Cerium, $Ni/Ce/Al_2O_3$ and Aluminium Oxide doped with Calcium, Ca/Al_2O_3. The reactor used was tubular reactor type; quartz reactor which was then placed in tubular furnace for heating purposes. The temperature for the pyrolysis to take place efficiently is at 700 ^oC. At higher temperature, the gas produced is higher. Pre-test of pyrolysis by using Thermo gravimetric Analysis (TGA) was done first prior to experimental lab scale was carried out. The production of gas can be determined from the pre-test. From the analysis, POF has lower solid residue content with only 18.33 wt% than 22.78 wt% of EFB. It seems that POF has better performances than EFB due the low content of char. Thus, the experimental lab scale was carried out by using POF samples. The production of fuel gas from this process was recorded and analysed by using portable gas analyzer and thermo gravimetric analysis (TGA). The result was analysed based on the fuel gas produced. From the analysis, Ca/Al_2O_3 produces high CO_2 and has higher percent of solid content compared to $Ni/Ce/Al_2O_3$. In the experiment, $Ni/Ce/Al_2O_3$ produces more fuel gas compared to Ca/Al_2O_3. It can be deduced that the application of $Ni/Ce/Al_2O_3$ produces more gas than non-catalytic process.

ABSTRAK

Gas bahan api boleh dihasilkan daripada proses pirolisis bio jisim. Gas bahan api adalah tenaga bersih dan boleh diperbaharui oleh sebab itu, ia menjadi tenaga yang sangat sesuai yang boleh menggantikan bahan api fosil sebagai contoh hidrogen dan metana. Kuantiti sisa pertanian yang banyak terutamanya di Malaysia seperti sisa kelapa sawit menjadikan proses ini lebih menarik untuk dikaji. Kajian ini bertujuan untuk menghasilkan gas bahan api yang tinggi dengan pemangkin rintangan kok. Sisa kelapa sawit digunakan sebagai sampel dalam kajian ini iaitu tandan kosong (EFB) dan serat kelapa sawit (POF). Pemangkin yang digunakan adalah alumina nikel, disalutkan dengan Serium, $Ni/Ce/Al_2O_3$ dan Aluminium Oksida disalutkan dengan Kalsium, Ca/Al_2O_3. Reaktor yang digunakan adalah jenis reaktor tiub; reaktor kuarza yang akan ditempatkan di dalam relau tiub untuk tujuan pemanasan. Julat suhu pirolisis yang efisien adalah pada 700 ^oC. Pada suhu yang lebih tinggi, gas yang dihasilkan adalah lebih tinggi. Ujian pra pirolisis dengan menggunakan Thermo gravimetrik Analisis (TGA) dilakukan terlebih dahulu sebelum eksperimen berskala makmal telah dijalankan. Dengan cara itu, pengeluaran gas boleh diramal dari ujian pra ini. Daripada analisis, POF mempunyai kandungan sisa pepejal yang lebih rendah dengan hanya 18.33 % berat daripada 22.78 % berat EFB. Didapati POF mempunyai prestasi yang lebih baik daripada EFB kerana mengandungi arang yang rendah. Oleh itu, skala makmal eksperimen telah dijalankan dengan menggunakan sampel POF. Pengeluaran gas bahan api dari proses ini direkodkan dan dianalisis dengan menggunakan gas penganalisis dan termo gravimetrik analisis (TGA). Produk eksperimen telah dianalisis berdasarkan gas bahan api yang telah dihasilkan. Berdasarkan analisis, Ca/Al_2O_3 menghasilkan CO_2 dan kandungan arang yang lebih tinggi berbanding dengan $Ni/Ce/Al_2O_3$. Dalam eksperimen ini, $Ni/Ce/Al_2O_3$ menghasilkan lebih gas bahan api berbanding Ca/Al_2O_3. Kesimpulannya, penggunaan $Ni/Ce/Al_2O_3$ menghasilkan lebih gas daripada proses bukan pemangkin.

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LIST OF SYMBOLS

%	Percent
<	Less than
>	More than
µ	Micro
cm	Centimetre
g	Gram
min	Minute
MJ/m^3	Mega Joule per metre cube
ml/min	Millilitre per minute
mm	Millimetre
^oC	Degree celcius
$^oC/min$	Degree celcius per minute
psi	Unit of pressure
wt%	Weight percent
$Ca(OH)_2$	Calcium hydroxide
Ca/ Al_2O_3	Calcium aluminium oxide
$CaCO_3$	Calcium carbonate
CaO	Calcium oxide
CeO_2/SiO_2	Cerium oxide with silicon oxide
CH_4	Methane
CO_2	Carbon dioxide
H_2O	Water
Ni	Nickel
Ni/ Al_2O_3	Nickel aluminium oxide
$Ni/Ce/Al_2O_3$	Nickel cerium aluminium oxide
Pt	Platinum
Pd	Palladium
Ru	Ruthenium
$Ru/CeO_2/SiO_2$	Ruthenium cerium oxide silicon oxide

LIST OF ABBREVIATIONS

EFB	Empty Fruit Bunch
FFB	Fresh Fruit Bunch
MPOB	Malaysian Palm Oil Board
MSW	Municipal Solid Waste
POF	Palm Oil Fibre
POME	Palm Oil Mill Effluent
TGA	Thermo gravimetric Analysis
WGS	Water Gas Shift

1 INTRODUCTION

1.1 Motivation and statement of problem

Fuels that we used nowadays come from the hydrocarbon that is formed for hundreds of years ago. This energy resource is not renewable and is depleting. Hydrocarbons are also causing green house effect and bad environmental issue. Emissions from fossil fuel usage significantly degrade air quality all over the world. The resulting carbon byproducts are substantially changing the world's climate.

Unfortunately, the demand for energy is growing but the raw materials for the fossil fuel economy are diminishing. If oil, coal, and natural gas supplies are not replenished as it is consumed, so an alternative must be found. Because of that, people have been searching for new energy source that is renewable, clean for the environment, free and have the same promising quality as fossil fuels.

Hydrogen and methane are one type of fuel gas. It is a type of energy that is renewable, clean, safe and economically competitive with gasoline or diesel .Hydrogen also can help prevent the depletion of fossil fuel reserves .Hydrogen production plays a very important role in the development of hydrogen economy. One of the promising fuel gas production approaches is conversion from biomass, which is abundant, clean and renewable. Alternative thermo chemical (pyrolysis and gasification) and biological (biophotolysis, water–gas shift reaction and fermentation) processes can be practically applied to produce fuel gas. (Ni et al, 2006)

Pyrolysis is a process where oil and gas are produced from biomass. In Malaysia for instance, has a big agricultural industry and resulted to come with a lot of issue with the waste. Thus, pyrolysis of agricultural waste is able to create a new renewable energy that is safe, environmental friendly and economic. It also helps to reuse the agricultural waste. In this study, the sample is used based on the waste product from the palm oil agricultural industries.

To upgrade pyrolysis, catalyst can be added to enhance the production of the gas. But unfortunately, catalysts are exposed to problem of coking and tar formation. Tar

formation can decrease the function of the catalyst thus causing the production of gas or oil to be less. To overcome this problem, catalysts are doped with metal transition to avoid the formation of tar thus creating a good coking resistant metal.

Production of fuel gas by using catalytic pyrolysis has been done for a long time. Fuel gas production of pyrolysis is always being compared with other production by using steam reforming and gasification. A review on hydrogen production of steam reforming and pyrolysis shows more hydrogen yield using pyrolysis compared to steam reforming. (Mann et al, 1997) And the review of hydrogen production technologies in Malaysia shows, biomass pyrolysis has the lowest cost in the production of fuel gas energy. (Khan et al, 2010).

1.2 Objectives

The objective of this research is to study the effect of catalyst on fuel gas production.

1.3 Scope of this research

This pyrolysis was carried out by using palm oil fibre and EFB as the feedstock. This was because both of it are low priced and abandoned material from palm oil milling process (Azizan, et.al, 2009). The catalyst used was $NiCeAl_2O_3$ and $CaAl_2O_3$. To avoid the coke formation on the catalyst, two metal transition are going to be use to test for their performances with the catalyst which are Calcium and Cerium. The gaseous product from the pyrolysis was analyzed by using gas analyzer. The element of composition of the gaseous was identified. The best coke resistance metal and the high yield of fuel gas produced is the main target in this research.

1.4 Significant and Rationale

As the fossil fuel prices has risen day by day due to the depleting resources, it is best to find another fuel sources that can replace the non renewable energy. By producing fuel gas using pyrolysis process, biomass waste can be turned from pollution problem into

energy supply. This type of energy will have lower cost compared to the fossil fuels due to the abundant availability of the raw material which is agricultural waste. This study also can help to identify the potential catalyst to be used in pyrolysis that able to produce fuel gas.

2 LITERATURE REVIEW

2.1 Overview

This thesis presents the experimental study of catalytic pyrolysis using agricultural waste. In this topic, the study is focusing on the effects of catalyst type towards the production of fuel gas.

2.2 Introduction

Hydrogen is an attractive clean energy carrier. Production of hydrogen by steam reforming of natural gas is the most widely used in industrial process because of its economic feasibility. However, reforming process produces significant amount of carbon dioxide and thereby contributes to the global warming. The inter-related problems between energy and environmental issues are among the biggest challenges today, in particular energy sustainability and carbon emission from fossil fuels. For this reason, renewable biomass becomes an attractive alternative energy resource. There is abundant biomass on the earth, such as energy crops, agricultural residues, forestry residues, industrial and municipal wastes, etc. Since biomass absorbs the same amount of carbon during its grow-up as it consumed as fuel, production of hydrogen from biomass could be critical for the energy and environmental sustainability. Extensive investigations of hydrogen production from biomass have been carried out in the past decades .There are several technologies available for the production of hydrogen from biomass, such as syngas from gasification, hydrogen, bio-oils and char from pyrolysis, and hydrolysis of cellulose for sugar monomer. (Qinglan et al, 2010)

2.3 Renewable Energy

Fossil fuels have become the source of energy for a long time. Either natural gas or even crude oil, engineers have been fought to find more gas wells around the world to ensure the sustainability of fossil fuels. However, sooner or later, there will be no more gas wells. Fossil fuel is one type of non renewable energy which is the energy that cannot be reuse or reproduce due to its limited quantity and will vanish fifty to sixty years from now. Other types of non renewable energy are coal and nuclear. Apart from not being

able to regenerate in a short time, these types of energy are not environmental friendly. Non-renewable sources release toxic gases in the air when burnt which are the major cause for global warming. Last but not least, since the non-renewable energy will be depleted, the prices for the energy are increasing throughout the days.

On the other hand, renewable energy is easily regenerated. This is unlike fossil fuels which are perishable once used. The sun, water, wind and biomass are available in the abundant quantity and free to use. The non-renewable sources of energy that we are using are limited and are bound to expire one day. Renewable sources have low carbon emissions, therefore they are considered as green and environment friendly. Renewable helps in stimulating the economy and creating job opportunities. Nowadays, a lot party has shown interests in the renewable energy including the private company and the government bodies. There are a lot of incentives givens to any party that try to come out with new renewable technology such as solar panel or hydrogen energy.

2.4 Biomass

Biomass is biological material derived from living or in the context of energy it is often used to mean plant based material. Biomass is carbon based and is composed of a mixture of organic molecules containing hydrogen, oxygen, nitrogen and also small quantities of other atoms. Biomass contains stored energy. That's because plants absorb energy from the sun through the process of photosynthesis. When biomass is burned, this stored energy is released as heat. Burning biomass releases carbon dioxide. However, plants also take carbon dioxide out of the atmosphere and use it to grow their leaves, flowers, branches, and stems. That same carbon dioxide is returned to the air when the plants are burned.

2.4.1 Biomass in Malaysia

The main sources of biomass in Malaysia are domestic wastes (MSW), agricultural residues, animal wastes, effluent sludge which is waste water and wood chip. Figure 2-1 shows the overall biomass in Malaysia. Based from the figure, it is shown that agricultural wastes are the biggest biomass source in Malaysia compared to municipal waste.

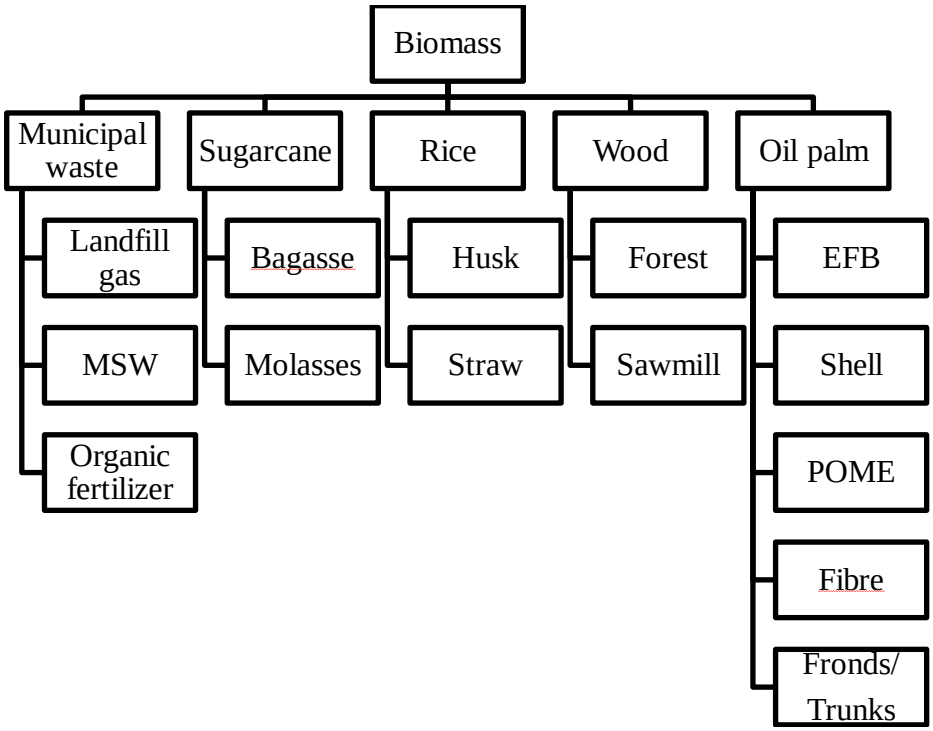

Figure 2-1 : Biomass in Malaysia
(Source: STAR Graphic 2012)

Agricultural waste is one form of biomass which is readily available but unfortunately it is largely not utilized in energy recovery schemes. (William and Nugranad, 1999). Most of the wastes are usually used for other purposes. For example, Oil Palm Fibres are used to make various fibre composites such as furnitures, infrastructures, and mattress. According to MPOB (2009), Malaysia produced 17.86 million tonnes of crude palm oil in year 2009 alone. This data derived from 100 million tonnes of EFB which produce 25 million tonnes of oil palm fibre (Hoong Chan Trading, 2009). It would be such a waste if these wastes are not tested for energy recovery process. The potential of agricultural residues for energy production has been investigated by many researchers (Perez and Cortez, 1997; Natarajan et al., 1998; Liet al., 1999; Di Blasi et al., 1999; Sensoz et al., 2001) and the results are very encouraging

Empty Fruit Bunch (EFB) is the waste component come after Fresh fruit Bunch (FFB) which were thrown away from palm oil mill. In the palm oil milling process, one tonne of FFB produce about 0.22 tonne of EFB (Wingkis, 1998).

Table 2-1 : Availability of EFB in Sabah

(Source: Malaysia Oil Palm Statistics 2008)

Year	FFB*	EFB*
2003	24,200,332	5,324,073
2004	24,939,817	5,486,760
2005	27,803,370	6,116,741
2006	28,632,381	6,299,124
2007	29,425,177	6,473,539
2008	30,698,689	6,753,712

*in unit of tonnes

According to the table above, the increment of EFB occurs each year by approximately 3%. The utilization of fresh EFBs as much has increased extensively, especially in oil palm, rubber and cocoa estates. The practice of placing EFBs on the soil surface has brought economic benefits as it enhances vegetative growth and increased production (Yeow et al., 1985).

EFB from oil palm were initially utilized as fuel. It has a moisture content of 60 - 65%. Before it can be used as a fuel for the boilers, the moisture has to be reduced to 40% or less. This is achieved through the use of a special screw press, which presses out the moisture from the EFB. According to Lim and Ratnalingam (1980), EFB can produce total energy as much as 2 568 calorie/kg (screw pressed EFB), if used as a fuel.

2.4.2 Biomass Utilization

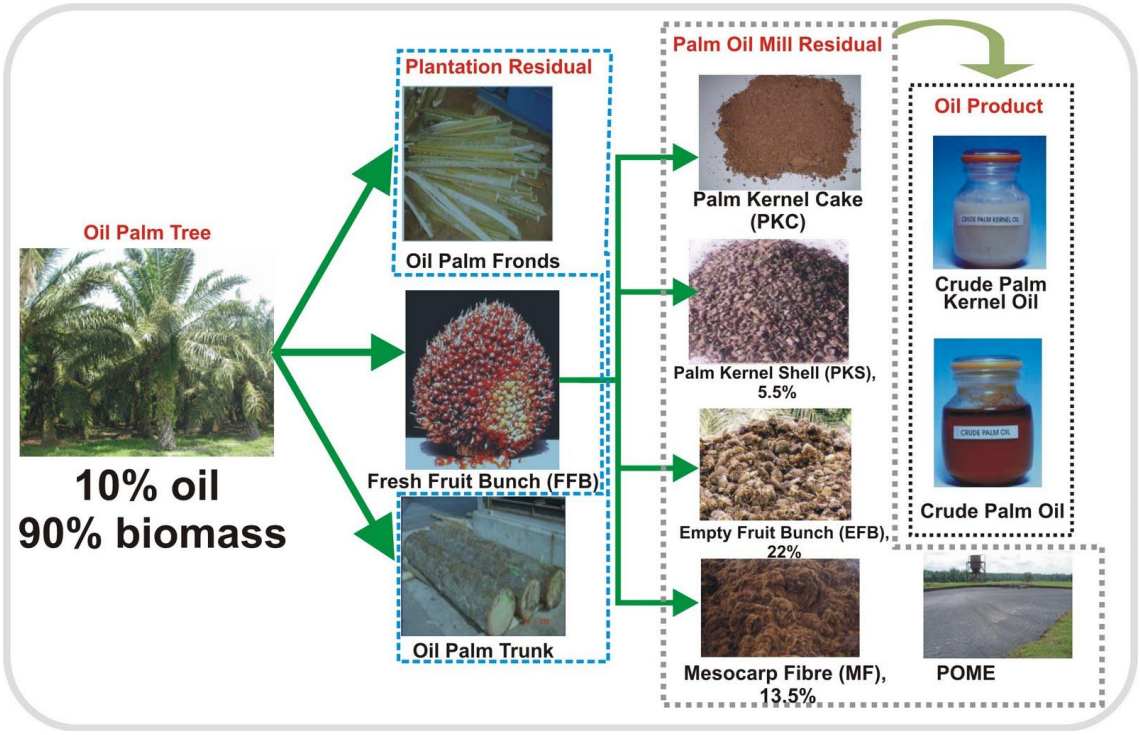

Figure 2-2: Utilization of Biomass

http://jfe-project.blogspot.com/2010_04_01_archive.html (Adopted 2012)

Figure 2-2 shows the production and the usage of the oil palm tree from the plant until oil product. It is stated that only 10% oil can be produced from an oil palm trees but up to 90% of biomass is not economically and fully utilized. Thus, it would be such a waste to not using this waste to make a more productivity use.

2.5 Thermal Conversion

2.5.1 Production of Fuel Gas

Figure 2-8 illustrates the different routes which can be adopted to produce hydrogen from biomass, including gasification to produce syn-gas, pyrolysis to produce bio oils and hydrolysis of cellulose to produce sugar.

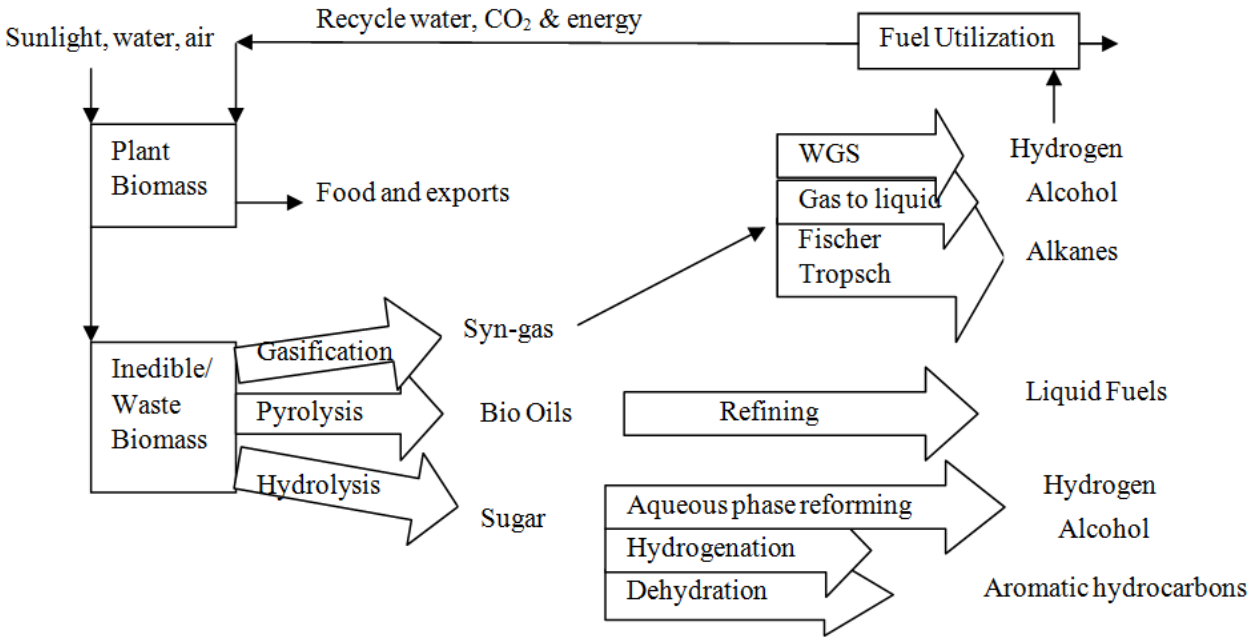

Figure 2-3 : Hydrogen and liquid fuels production from biomass sources. (Huber and Dumesic, 2006)

Syn-gas can be converted to hydrogen by water gas shift (WGS) reaction; however, any remaining CO must be removed from the gas stream. This can be achieved by preferential oxidation of CO. Pyrolysis bio-oil can be converted to liquid fuel but the processes are complex and the conversion is low. Hydrogen can be produced from the bio-oil by auto thermal reforming with high conversion efficiency, especially with the use of catalytic membrane reactors. Aqueous phase reforming can be used to convert sugars and sugar alcohols, such as sorbitol, to produce hydrogen.

2.5.2 Pyrolysis

Pyrolysis is the devolatilization of volatile matter in inert medium to produce pyrolytic liquids, solid char and gaseous fuel. In simple words, it can also be said that pyrolysis is a process which can generate a char, oil and gas product from anything that have a

potential end use. (William and Nugranad ,1999) So it means that, pyrolysis process enables biomass or non-biomass waste to be processed into oil, gases and char. But this product may vary depending on the types of samples used.

The catalytic pyrolysis is the pyrolysis using the help of catalyst. Most pyrolysis is designed for biofuels production. However, hydrogen can be produced directly through fast or flash pyrolysis if high temperature and sufficient volatile phase residence time are allowed. The pyrolysis products can be divided into a volatile fraction, which consists of gases, vapors, tar components and a carbon rich solid residue (Demirbas, 2002).

Some research has proved that by adding catalyst onto the process, the production of oil and gas yield can increase far more compared to non-catalytic pyrolysis and also enables the oil to be upgraded thus having the same quality with petroleum fuel. (William and Nugranad, 1999). Catalyst can be upgraded in many ways. Using catalyst can upgrade production of pyrolysis liquid by using fast pyrolysis which can produce up to 75% of bio-oil liquid(Czernik et al., 2003). One of it is by using zeolite type catalysts at atmospheric pressure to dehydrate and decarboxylate the oil (Brown and Holmgren, 2009). But zeolites also have all sorts of type and the main zeolite catalyst used for upgrading biomass pyrolysis is the hydrogen form of the zeolite, ZSM-5. This is because it has a strong acidity, high activities and shape selectivity which can convert the oxygenated oil to a hydrocarbon mixture in the C1 to C10 range which resulting a highly aromatic compounds similar in composition to gas (William and Horne, 1997).

Table 2-2: Hydrogen yields and energy ratios obtained from various processes (Demirbas, 2001)

Processes	H_2 yield	Energy ratio
Pyrolysis + steam reforming	12.6	91
Gasification +WGS	11.5	83
Biomass + steam + heat	17.1	124

Table 2-2 illustrates the H_2 yields that can be obtained from biomass using various processes and the theoretical maximum including the ratios of heating values of the product hydrogen with respect to the biomass feed (Demirbas, 2001)

2.5.3 Type of Pyrolysis

There are four types of pyrolytic reactions, which are differentiated by temperature and the processing of residence time of the biomass.

I. Slow Pyrolysis

Conventional or slow pyrolysis is characterized by slow biomass heating rates, low temperatures and lengthy gas and solids residence times. Depending on the system, heating rates are about 0.1 to 2.0 ^{o}C per second and prevailing temperatures are around 500 ^{o}C. Gas residence time may be greater than five seconds. During conventional pyrolysis, the biomass is slowly devolatillized, hence tar and char are the main products.

II. Flash Pyrolysis

Flash Pyrolysis is characterized by moderate temperatures exist 400-600 ^{o}C and rapid heating rates >2 ^{o}C/s. Vapor residence times are usually less than two seconds.

III. Fast Pyrolysis

The only difference between flash and fast pyrolysis is heating rates. Heating rates are between 200 and 10 ^{o}C per second and the prevailing temperatures are usually higher than 550 ^{o}C. Due to the short vapor residence time, products are high quality, ethylene rich gases that could subsequently be used to produce alcohols or gasoline. The production of char and tar is considerable less during this process.

IV. Catalytic Pyrolysis

Pyrolysis oil consists of a complex mixture of aliphatic and aromatic oxygenates and particulates. It is very viscous, acidic and unstable liquid with relatively low-energy density compared to conventional fossil oil. Such poor quality of the bio oil requires costly post treatment and makes complete process economically less attractive.

2.5.4 Type of Reactor

There are several types of pyrolysis reactor. The most common types are bubbling fluidized bed, circulating fluidized bed, rotating cone pyrolyzer and ablative pyrolyzer. Each type has their own design and applications.

I. Bubbling fluidized bed

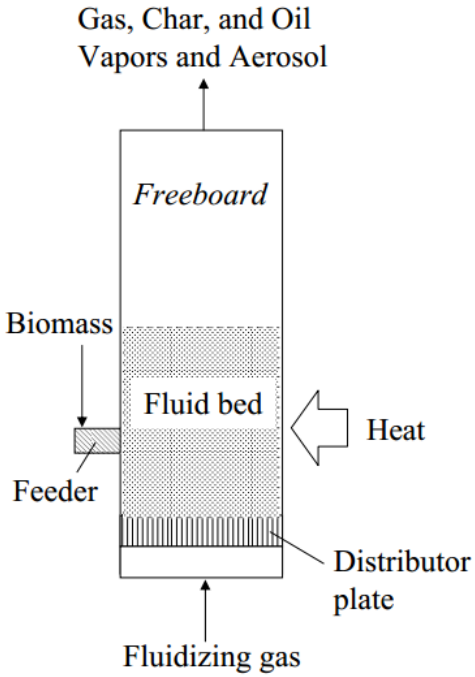

Figure 2-4 : Bubbling Fluidized Bed

Bubbling fluid beds, as shown in Figure 2-3, usually referred to as just fluid beds as opposed to circulating fluid beds. It have the advantages of a well understood technology that is simple in construction and operation, good temperature control and very efficient heat transfer to biomass particles due to high solids density. Heating can be achieved in a variety of ways .However, heat transfer to bed at large-scales of operation has to be considered carefully due to scale-up limitations of different methods of heat transfer.

II. Circulating fluidized beds/transport reactor

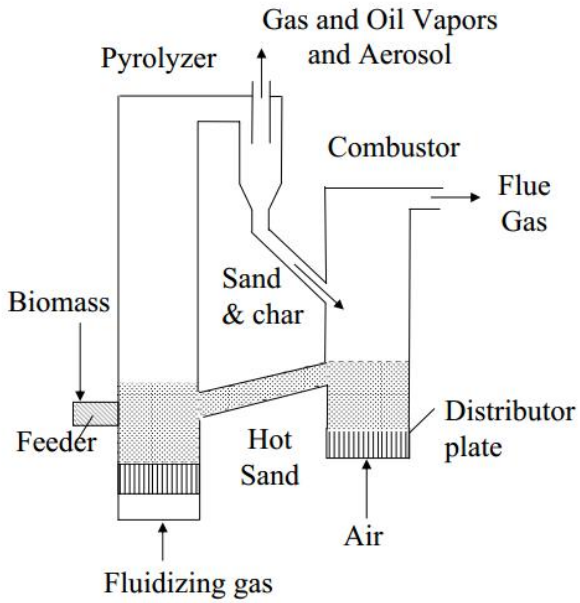

Figure 2-5 : Circulating fluidized beds

Figure 2-4 is a circulating fluidized bed pyrolyzer. This type is similar to bubbling fluidized bed reactors but have shorter residence times for chars and vapors. The short residence times encountered in the reactor result in higher gas velocities, faster vapor and char escape and higher char content in the bio-oil than bubbling fluidized beds. However, they have higher processing capacity, better gas-solid contact and improved ability to handle solids that are more diffi-cult to fluidize but are less commonly used. The heat supply typically comes from a secondary char combustor.

III. Rotating cone pyrolyzer

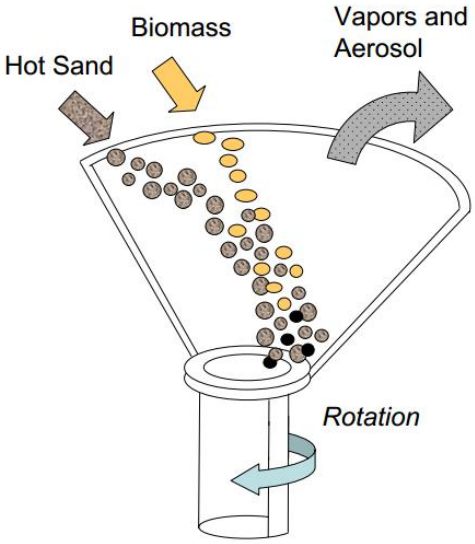

Figure 2-6 : Rotating cone pyrolyzer

In a rotating cone pyrolysis reactor, biomass particles at room temperature and hot sand are introduced near the bottom of a cone at the same time. They are mixed and transported upwards by the rotation of the cone as shown in Figure 2-5. Rapid heating and short gas phase residence times can be easily achieved in this reactor.

IV. Ablative pyrolyzer

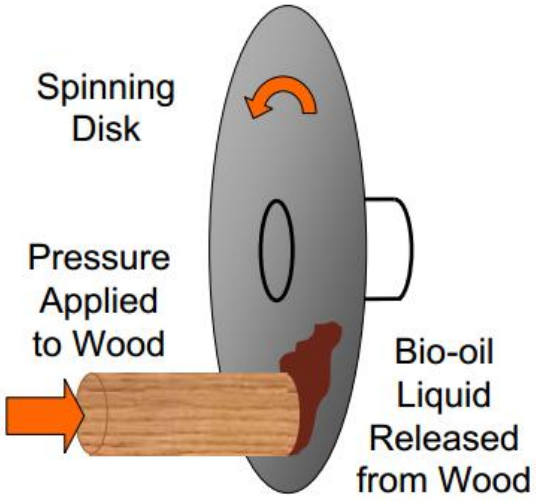

Figure 2-7 : Ablative pyrolyzer

Ablative pyrolysis (Figure 2-6) is different in concept compared to the other methods of fast pyrolysis. In other methods, the rate of reaction is limited by the rate of heat transfer through a biomass particle, which is why small particles are required. In ablative pyrolysis heat is transferred from the hot reactor wall to "melt" wood that is in contact with it under pressure. As the wood is mechanically moved away, the residual oil film both provides lubrication for successive biomass particles and also rapidly evaporates to give pyrolysis vapors for collection in the same way as other processes. The rate of reaction is strongly influenced by pressure, the relative velocity of wood on the heat exchange surface and the reactor surface temperature.

2.6 Catalyst

One of the methods to increase the H_2 yield is to apply catalytic pyrolysis. (Chen et al., 2003) Hydrogen can be effectively produced from biomass pyrolysis with the assistance of catalysts at wide ranges of temperatures. High temperature favour total gas yield containing hydrogen. Catalyst load has an obvious influence on the hydrogen containing gas yield. (Chen et al., 2003) The usage of catalysts in the pyrolysis helps in improving the yield and quality of gas. It has been proven that the highest yield of hydrogen 12.65 wt% and 91 % energy conversion efficiency were obtained from biomass pyrolysis with adding of catalyst. Although hydrogen yield from the direct pyrolysis of biomass is quite low, it was known that the gas yield, could be highly improved by adding catalyst. (Yang et al., 2006)

2.6.1 Coking Problem

One of the major issues in biomass pyrolysis is the formation of tar, soot, coke and other carbon compounds in the reactor (Figure 2-7). Depending on the process conditions, like pressure and temperature, different forms of coke may appear, some of which are more hazardous to the process than others. To ensure trouble free operation of the reformer, it is essential to control the soot formation in all process conditions including process shut-downs, start-ups and disturbances.